

Hard Work and Light Experience: Early Steps in Photochemistry

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Abstract: The author describes his early steps as an independent researcher at the University of Geneva. His interest in synthetic organic photochemistry came from his past non-experience at the Universities of Geneva and Stanford, where he worked mainly on natural product synthesis and transition-metal catalysis.

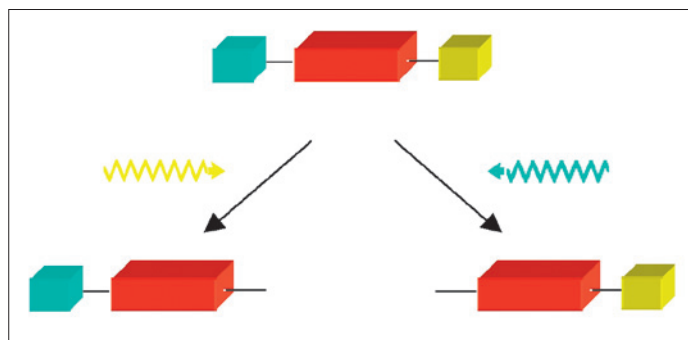
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It is often heard that the postdoc time is the best period in a scientific career, because as a PhD one has to worry about producing enough results to fill a thesis, while for the few crackpots who want to continue an academic career, the stress continues: they have to identify a research topic which is a) far away from the PhD theme but b) within their realm of competence, c) completely new, but d) with precedent otherwise they will be considered insane, e) risky, but f) non risky! Despite the above, the postdoc time is in fact a unique period, where it really is possible to initiate a new line of research, without heavy heritage from previous activities and without the temptation to make serendipitous findings appear as results of a well planned strategy.

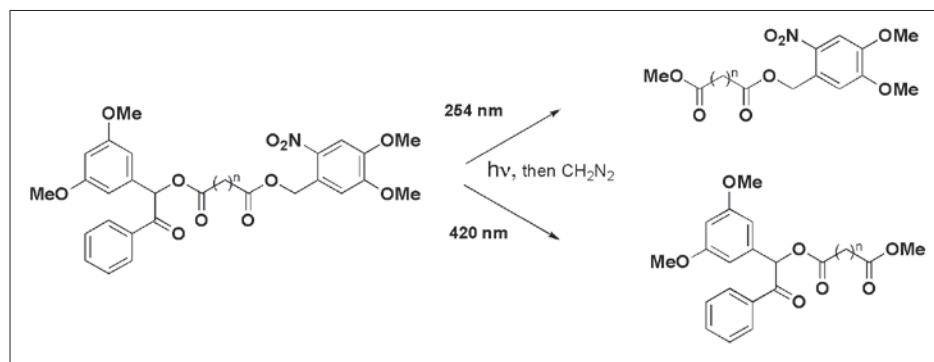
It was in this state of mind that I started in October 1998 in Geneva, with the task of turning into reality a proposal which I had just submitted to the SNF: is it possible to affect the outcome of a chemical process by an external stimulus? Traditionally, a chemical reaction is started by mixing the reactants in a suitable container, perhaps with some additives, catalysts and a solvent, after the desired temperature is established. Once the flask is sealed, the reaction starts and gives a product, preferentially in a selective way. If the same ingredients are mixed again any time later, one expects to get the same result (...of course, a pragmatic organic chemist knows that it is rarely the case, but somehow or other develops an intellectual resistance to this blatant violation of scientific principles). In other words, the initial conditions fully determine the outcome of the process: the reactants contain the information on how they will end up. On the other hand, it might be desirable for the chemist to be able to influence the outcome: in a system, which does not contain enough information to fully determine its future, one could think of transmitting in real time the missing information. We envisioned that light might be a good vector to transmit this information, as it has several tunable properties (such as its intensity, its wavelength and its polarization). An example of this strategy is shown in Scheme 1.

Driven by the common tendency of young and enthusiastic researchers to consider their own ideas as incredibly cool, I started working at the bench on the afternoon of October 1st, at the same time as my friend and colleague *Alex Alexakis* moved his group from Paris, and started unpacking. Since I had nothing to unpack and the clock was ticking, I was already mixing reagents under the incredulous eyes of Alex's students, wondering who was the guy in a lab coat who was not helping putting the champagne in the fridge for the welcome party. At this point it is important to mention that I benefited for many years from Alex generosity, since I had no separate labs, and my budget for the year had already been eaten up by the connection fee of my private computer to the University network. Without his help, nothing that followed would ever have been possible! As a matter of fact, the whole project was on the brink of being a non-starter, when, in the midst of frantic measurements of photolysis reaction rates at various wavelengths to show that my idea was indeed sound, I received a call from the SNF urging me to withdraw my request for funding. The idea was dubbed too speculative and doomed by very fundamental flaws (rapid vibrational energy redistribution would result in the loss of the information on the site where excitation had occurred). Furthermore, I had neither formal training in photophysics and photochemistry, nor a track-record in independent scientific publications.



Scheme 1.

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Scheme 2.

Tenacity is definitely a necessary trait for a researcher, and such a setback did not deter me from pursuing this project. The large amount of kinetic data that I had accumulated provided the basis of a proof-of-principle paper, which was published in early 2000.^[1] Despite the low selectivity of our system (two differently substituted *ortho*-nitrobenzylic esters) and the fact that our test reaction verified only the *inter*-molecular mode, I succeeded to convince the SNF to give me some funding, which marked the real start of my independent research career. With this grant, I finally could move into my own lab and office (the latter was actually a former chemicals storage room, and it took me several weekends to thoroughly clean, paint, carpet and furnish it to a decent state) and hire my first graduate student, *Céline Helgen*. The impact of the first coworker in a group in construction is absolutely crucial, and I was incredibly lucky to benefit from on her hard work and her sense of risk, having dared to join me. While pursuing myself the work on wavelength-dependent

photochemical reactions, Céline started to work on photoinduced acylations and rapidly produced material for publication, which helped to convince the SNF that a second graduate student would be necessary.^[2,3] *Aurélien Blanc* thus joined our group one year later. In the mean time, we finally achieved the long expected breakthrough in wavelength-selective reactions, as we could show that a diester could be cleaved selectively at either terminus, depending on the wavelength of the incident light beam. This proved not only that our idea was valid, but also that it worked in the *intra*-molecular mode (Scheme 2). In fact, the results seemed too good to be fully trusted, and Aurélien's first task was to double check my own work. Aurélien's fantastic experimental skills produced even better results than mine, paving the way for a series of articles in *Angewandte Chemie*, *J. Org. Chem.* and finally *J. Am. Chem. Soc.* on what we dubbed *chromatic orthogonality*, i.e. the orthogonality arising from the color of a light beam (the analogy comes from the *chemical orthog-*

onality, where the selectivity arise from specific reaction conditions).^[4-6] Thank to the formidable work of these two graduate students, our research program was now on good tracks, and soon I received the good news that I had been awarded an SNSF professorship, albeit on the condition that I would move to a different university. In the fall of 2002, exactly four years after starting in Geneva, I moved to the University of Fribourg, where the adventure continued, although under different premises. As a professor, the teaching and administrative duties increased gradually, taking me away more and more from the lab, up to the point where I sadly had to renounce my own private bench.

Looking back on these early days, I am infinitely indebted to the University of Geneva, who trusted me enough to give me the opportunity to start my own independent research. And to be fully honest, it is always with a touch of nostalgia that I remember those intense and stressful days. Stressful, they definitely were: making the chemistry work and finding a more stable job were not insignificant burdens on my mind. But on the other hand, being at the bench and making the things happening is something that I miss.

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